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Combining X-ray and Electron Based *in situ* Characterization of Catalysts

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To understand the function of catalysts for heterogeneous catalysis and improve catalytic properties, a fundamental insight into structure-functionality relationships is required. As catalysts may change their structure with respect to the environment, it is essential to investigate the catalysts under reaction conditions. Furthermore, structural and compositional information have to be acquired on different length scales[1] and such *in situ* studies require dedicated complementary techniques. *In situ* X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) are eminent to follow the average catalyst's structural (local and global) and electronic changes during synthesis and reaction conditions[2]. In order to follow the dynamics (stability, topography, etc.) of the surface and interfaces, imaging is often the solution[3]. Nanoscale imaging and spectroscopy of catalysts in a gaseous environment is traditionally performed in an environmental transmission electron microscope (ETEM). TEM gives insight in the atomic changes during reaction, however it is restricted to relatively low pressure (<~1 kPa) and a thin sample (<~100 nm)[4]. Spatially resolved information on the meso scale (50 nm–1 µm) can be obtained by X-ray microscopy, which enables *in situ* studies at both ambient and elevated pressure[5]. Furthermore, due to the much higher penetration depth of X-rays compared to electrons, X-ray based characterization techniques are more suited for realistic sample and conditions.

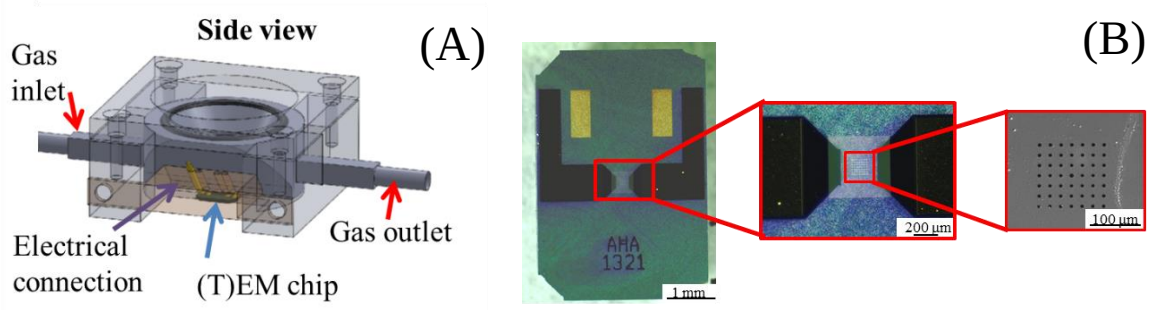

Figure 1. *A) Sketch of in situ cell used for x-ray Ptychography. B)* Optical micrograph of a Protochips® Aduro E-Chip with SiN membrane[5].

This contribution illustrates how catalyst properties can be elucidated by the combination of X-ray and electron based methods in general. One example highlighted combines X-ray imaging with ETEM studies. By use of a special designed *in situ* cell (Figure 1A) a bifunctional Cu/ZnO@zeolite core-shell catalyst for direct production of methanol was studied with hard X-ray microscopy (X-ray ptychography)[6]. The cell is based on a TEM heater chip from Protochips (Figure 1B), which enables *ex situ* electron microscopy imaging before and after reaction[5]. The complementary nature of *in situ* hard X-ray ptychography and electron microscopy was applied to study the stability of the core-shell catalyst in a hierarchical manner at different length scales during reduction and oxidation treatments. *In situ* Ptychograms of the Cu/ZnO@zeolite core-shell catalyst is shown in Figure 2. The study reveals a stable core-shell interface at 250°C, although reduction of the Cu containing core

material led to a shrinkage of the particles on the nanometer scale. At further heating to 350°C changes on the µm scale were observed.

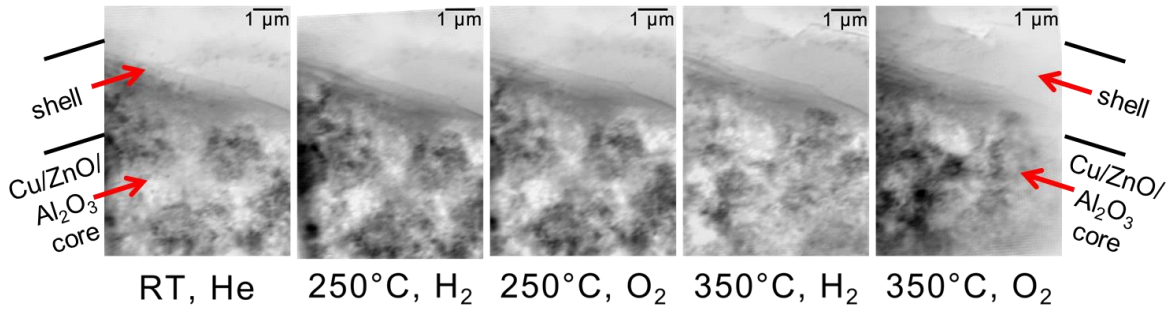

Figure 2. *In situ* ptychograms (phase contrast) of a thin slice of a Cu/ZnO@zeolite core-shell catalyst at room temperature in He, 250°C in H_2, 250°C in O_2, 350°C in H_2, and 350°C in O_2 , respectively [6].

The results underline the need for complementary techniques and highlight the potential of these for application in catalysis.

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